Fixed nitrogen atoms in the SiO2/SiC interface region and their direct relationship to interface trap density

doi: 10.1063/1.3659689

Fixed nitrogen atoms in the SiO_2/SiC interface region and their direct relationship to interface trap density

R. Kosugi,[1,a)] T. Umeda,[2] and Y. Sakuma[1]
[1]*Advanced Power Electronics Research Center (ADPERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8568, Japan*
[2]*Institute of Applied Physics, University of Tsukuba, Tsukuba 305-8573, Japan*

(Received 29 June 2011; accepted 20 October 2011; published online 4 November 2011)

Nitrogen atoms fixed in the SiO_2/SiC interface region were studied by x-ray photoelectron spectroscopy (XPS) and capacitance-voltage (C-V) measurements. A thin oxide film (<5 Å) formed during annealing in an NO atmosphere on a (0001) 4H-SiC surface, incorporating nitrogen atoms into the interface region. Even after complete removal of the oxide layer by etching in hydrofluoric acid, XPS spectra clearly showed a strong N 1 s peak, revealing the presence of fixed nitrogen atoms with an areal density of $10^{14}\,cm^{-2}$ in the interface region. To evaluate their influence on interface traps, metal-oxide-semiconductor capacitors were formed by deposition of a gate oxide layer. The fixed nitrogen atoms decrease the interface trap density after post-annealing at high temperature. © *2011 American Institute of Physics*. [doi:10.1063/1.3659689]

The low channel mobility of SiC metal oxide semiconductor field effect transistors (MOSFETs) is a critical issue for SiC power MOSFETs. Nitridation can be used to improve the channel mobility (μ_{ch}) in (0001) 4H-SiC MOSFETs.[1,2] Improvement of μ_{ch} is accompanied by a reduced interface trap density (D_{it}). This is because passivation and/or extinction of interfacial defects by nitridation decreases carrier trapping and coulomb scattering in an inversion layer. However, nitridation has two problems that affect the threshold voltage (V_{th}) of nitrided MOSFETs. One is the universal relationship between V_{th} and μ_{ch}: V_{th} decreases as μ_{ch} increases.[3] The other is the shift of V_{th} caused by application of a high electrical field to the gate oxide.[4] To overcome such a trade-off relationship between V_{th} and μ_{ch} and obtain reliable switching operations, greater insight into the role of nitrogen at nitrided SiO_2/SiC interfaces and the mechanism of μ_{ch} improvement by nitridation is required.

In this letter, x-ray photoelectron spectroscopy (XPS) measurements are used to determine the behavior of nitrogen atoms incorporated into the SiO_2/SiC interface region by NO annealing. A significant amount of nitrogen atoms remain in the SiO_2/SiC interface even after oxide removal by sustained etching in hydrofluoric acid (HF). To clarify their effect on SiO_2/SiC interface traps, metal oxide semiconductor (MOS) capacitors including such nitrogen atoms were examined using simultaneous high- and low-frequency capacitance voltage (CV) measurements.

N-type (0001) 4H-SiC substrates were purchased from Nippon Steel Company, and epitaxial layers were grown by Showa Denko Inc. The thickness and effective doping density ($N_d - N_a$) of the epilayer were 10 μm and $1.0 \times 10^{16}\,cm^{-3}$, respectively. Nitridation was performed at 800–1467 °C for 5 min under a 20% NO (balance Ar) atmosphere. A cold wall furnace[5] was used for high temperature nitridation above 1300 °C. The XPS apparatus consisted of a monochromatic Al kα light source ($h\nu = 1486.6$ eV) and an energy analyzer with a two-dimensional multi-channel plate detector. The take-off angle of the photoelectron was 37°. MOS capacitors were fabricated as follows. The thin oxide film that grew during pre-nitridation was removed by etching in 5% HF for 2 min, and then a 50 nm thick oxide film was deposited by plasma-enhanced chemical vapor deposition (PECVD). When deposited oxide is used as a gate insulator, post annealing is required to improve interface properties,[6] so the sample was annealed at 1200 °C for 30 min following oxide deposition. Both a gate electrode and back side substrate contact were formed by deposition of aluminum. D_{it} was evaluated at room temperature using a simultaneous high- and low-frequency CV technique. The sweep rate of all quasi-static CV measurements was fixed at 0.1 V/s.

Figures 1(a)–1(c) show Si 2p and N 1s XPS spectra of the as-grown epitaxial surface, and the same surface following nitridation at 1200 °C for 5 min, and after HF etching. The Si 2p spectrum in (a) shows a bulk SiC peak at 101.2 eV with no oxide-related peaks at a higher binding energy.[7] No peaks were observed in the N 1s spectrum, which indicates that the nitrogen concentration of the epitaxial layer ($10^{16}\,cm^{-3}$) is lower than the detection limit of the XPS. The Si 2p spectrum in (b) shows a new component at ~2.3 eV higher binding energy than the bulk peak, which is attributed to silicon dioxide (Si^{+4}).[7] From the ratio of peak intensities of the oxide and bulk SiC components in the Si 2p spectrum, the oxide thickness was estimated to be 4.3 Å. The N 1s spectrum of the nitrided surface shows a clear peak at 398.2 eV, indicating that a substantial amount of nitrogen has been incorporated at the SiO_2/SiC interface during nitridation.[8–10] Following these experiments, the thin oxide layer was removed by etching in HF and then XPS spectra were remeasured. The Si 2p spectrum in (c) does not show any components originating from the oxide; only the first epitaxial layer is present. Despite removal of the oxide, a strong N 1s peak is still observed. To confirm the absence of the silicon nitride layer on the substrate surface, etching in 50% HF for 10 min, which should remove the nitride,[11] was

a)Electronic mail: r-kosugi@aist.go.jp.

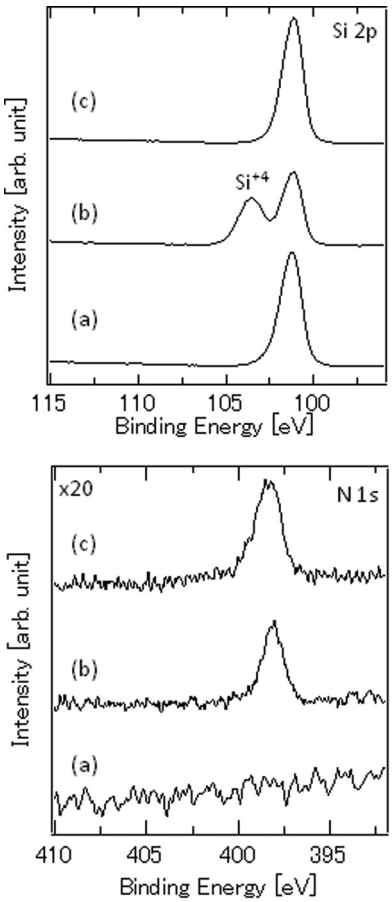

FIG. 1. Si 2p and N 1s XPS spectra of (a) as-grown epitaxial surface, and the same surface (b) after nitridation at 1200°C for 5 min, and (c) after a subsequent HF etching.

also performed on the sample. However, the N 1s peak was preserved. These results indicate that nitrogen atoms are fixed in the SiO_2/SiC interface region and remain unchanged by HF etching with different treatment times and concentrations.

The amount of fixed nitrogen atoms was estimated using the intensity ratio of Si 2p and N 1s signals. It was assumed that nitrogen atoms were located within the first bilayer (0.62 Å). The mean free paths (λ) of the Si 2p and N 1s photoelectrons in SiC were 14.5 Å and 12.9 Å, respectively, as calculated from the empirical relation, $\lambda = 15\sqrt{\mathrm{Ek}/1482}$Å (Ek: kinetic energy in eV). Consequently, the amount of nitrogen was estimated to be $1.68 \times 10^{14}\,\mathrm{cm}^{-2}$. Following oxide removal by HF etching, the intensity of the N 1s peak increased. If the most nitrogen atoms located on the oxide side are removed by HF etching, the intensity of the N 1s peak should decrease significantly. Therefore, the amount of fixed nitrogen is considered to be at least comparable to that in the oxide layer. Previously, it was believed that incorporated nitrogen atoms of $\sim 10^{14}\,\mathrm{cm}^{-2}$ were distributed in the oxide side of a nitrided SiO_2/SiC interface.[12] However, our findings suggest a new model that nitrogen atoms are not only embedded in the oxide layer but also fixed in the SiO_2/SiC interface region.

To confirm the effect of the fixed nitrogen atoms on the properties of the SiO_2/SiC interface, an n-type MOS capacitor was fabricated by oxide deposition on the nitrided surface that was etched with HF. Figure 2 shows the D_{it} distribution of the MOS capacitor as a function of the energy of the conduction band edge (E_c). As a reference, a MOS capacitor (a) was also formed using deposited oxide on a substrate without nitridation. Both capacitors were post-annealed under the same conditions after oxide deposition. Nitridation at 1467 °C for 5 min caused the number of interface traps to decrease drastically. At $E_c - E = 0.2$ eV, D_{it} was 20% of the reference sample. Because the only difference between the capacitors was nitridation, it is clear that the reduction in D_{it} was caused by the fixed nitrogen atoms in the SiO_2/SiC interface region of the nitrided sample.

The influence of nitridation temperature ($T_{nitridation}$) on the amount of fixed nitrogen and MOS characteristics was investigated, as shown in Figs. 3(a) and 3(b), respectively. Figure 3(a) shows N 1s spectra for different $T_{nitridation}$ of 800–1430 °C for 5 min. The inset shows the relationship between $T_{nitridation}$ and the areal density of fixed nitrogen. The straight line indicates a linear fitting. Interestingly, the areal density increased proportionally to $T_{nitridation}$. At the maximum $T_{nitridation}$ (1430 °C), the amount of fixed nitrogen atoms was $2.37 \times 10^{14}\,\mathrm{cm}^{-2}$. Figure 3(b) shows the D_{it} distribution of the four MOS capacitors corresponding to the four $T_{nitridation}$ examined above. The inset shows the relationship between $T_{nitridation}$ and the integral density of the interface traps (N_{it}), which was calculated from the integral of D_{it} over $Ec - E = 0.2$–0.5 eV. When $T_{nitridation} \geq 1100$ °C, a linear correlation between $T_{nitridation}$ and N_{it} was observed. This result indicates that the fixed nitrogen atoms are related to the reduction in D_{it} and that D_{it} decreases as the amount of nitrogen increases. In contrast, from 800 to 1100 °C, the fixed nitrogen atoms did not affect D_{it}, even though their amount almost doubled. This suggests that a threshold amount of nitrogen is required for effective reduction of D_{it}. Although the reason for such a threshold remains unclear at present, a similar trend has been reported in a previous study.[12]

Finally, the reason why nitrogen atoms incorporated into the SiO_2/SiC interface region are not removed by HF etching is discussed. There are two possible mechanisms that fix nitrogen atoms in the interface region. One is that

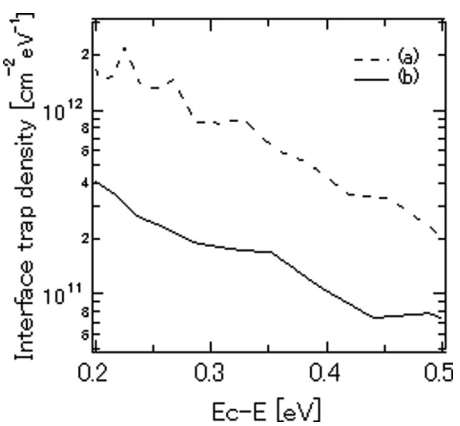

FIG. 2. Comparison of D_{it} for n-type MOS capacitors formed (a) without and (b) with nitridation at 1467 °C for 5 min. A gate oxide layer was formed by PECVD. Both MOS capacitors were etched in HF just before oxide deposition.

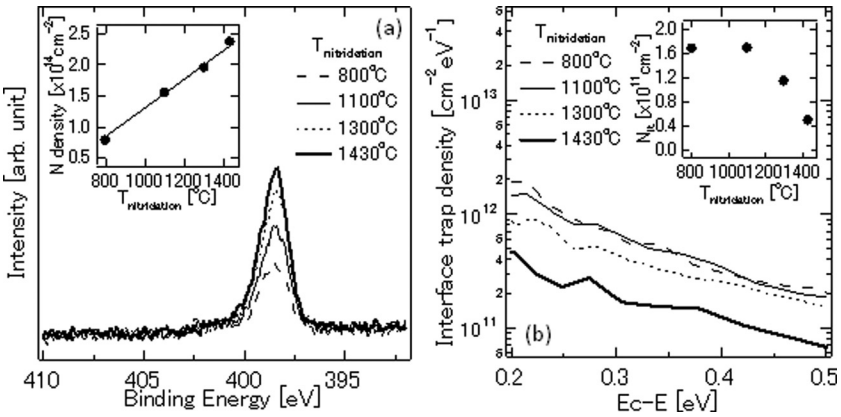

FIG. 3. (a) Dependence of the N 1s spectrum on $T_{nitridation}$. The inset shows the relationship between $T_{nitridation}$ and the nitrogen areal density. The solid line indicates a linear fitting result. (b) D_{it} distribution for n-type MOS capacitors formed at the corresponding $T_{nitridation}$ in (a). The inset shows the relationship between $T_{nitridation}$ and N_{it}, which is the integral of D_{it} at $Ec - E = 0.2$–0.5 eV.

nitrogen atoms form a special chemical bond so they become resistant to HF etching. This kind of chemical bonding may be formed during nitridation or HF etching.[13] For example, the formation of a perfect epitaxial monolayer of silicon oxynitride (SiON) on (0001) 6H-SiC surfaces after nitridation has been reported.[14] Because the proposed SiON structure lacks dangling bonds and survived after exposure to air for one month,[14] it may be possible that this special layer has chemical resistance to HF etching. However, the amount of fixed nitrogen estimated in this study (0.1–0.4 monolayers) suggests that a SiON layer may be produced in 10%–40% of the interface area during NO annealing. Because the amount of fixed nitrogen atoms was unchanged after etching in 50% HF, we can exclude the possibility that the low coverage of the SiON layer is caused by gradual etching of a perfect SiON monolayer.

Another possibility is that the fixed nitrogen atoms are incorporated into the SiC layer during nitridation. In another study where we applied electrically detected magnetic resonance to the channel region of (0001) 4H-SiC MOSFETs,[15] we found that nitrogen shallow donors were doped in the channel region after post-nitridation annealing. This result can be explained by supposing that some part of the fixed nitrogen atoms are incorporated into the SiC layer during nitridation where they occupy substitutional sites (i.e., carbon sites), and are activated as shallow donors. This model also provides a possible explanation for the universal relationship that an increase in μ_{CH} is associated with a reduction in V_{th}. That is, the doped nitrogen donors produce additional carriers that increase μ_{CH} as well as compensating for acceptors in the channel region, which reduces V_{th}.

In summary, investigation of nitrogen atomic profiles in the SiO_2/SiC interface by XPS measurements showed that a substantial number of nitrogen atoms (areal density of $10^{14}\,cm^{-2}$) remain fixed even after complete removal of the oxide layer. This was directly confirmed by the N 1s XPS spectra of a nitrided surface subjected to several subsequent HF etching treatments. CV measurements of MOS capacitors fabricated by oxide deposition on the nitrided surface revealed a significant reduction in D_{it} compared with the capacitor that was not subjected to nitridation. The amount of fixed nitrogen increases in direct proportion to $T_{nitridation}$, and D_{it} decreases as the amount of nitrogen increases. There are two possible causes for the presence of fixed nitrogen atoms in the SiO_2/SiC interface region. The first is that nitrogen atoms form chemical bonds in the SiO_2/SiC interface region that are resistant to HF etching (for example, formation of a SiON layer at the interface). Another possibility is that fixed nitrogen atoms are incorporated into the SiC layer where they function as nitrogen shallow donors. We believe that better understanding of the fixed nitrogen atoms in SiO_2/SiC interfaces will allow further improvement and precise control of the properties of these interfaces.

[1]G. Y. Chung, C. C. Tin, J. R. Williams, K. McDonald, R. K. Chanana, R. A. Weller, M. Di Ventra, S. T. Pantelides, L. C. Feldman, O. W. Holland, M. K. Das, and J. W. Palmour, IEEE Electron Device Lett. **22**, 176 (2001).
[2]J. R. Williams, G. Chung, C. C. Tin, K. MacDonald, D. Farmer, R. K. Chanana, R. A. Weller, S. T. Pantelides, O. W. Holland, M. K. Das, and L. C. Feldman, Mater. Res. Soc. Symp. Proc. **640** H3.5.1 (2001).
[3]A. Agarwal, A. Burk, R. Callanan, C. Capell, M. Das, S. Haney, B. Hull, C. Jonas, M. O' Loughlin, M. O'Neil, J. Palmour, A. Powell, J. Richmond, S. H. Ryu, R. Stahlbush, J. Sumakeris, and J. Zhang, Mater. Sci. Forum **600–603**, 895 (2009).
[4]A. J. Lelis, D. Habersat, G. Lopez, J. M. McGarrity, F. B. McLean, and N. Goldsman, Mater. Sci. Forum **527–529**, 1317 (2006).
[5]R. Kosgui, K. Fukuda, and K. Arai, Matter Sci. Forum **483–485**, 669 (2005).
[6]R. Kosugi, W. Cho, K. Fukuda, K. Arai, and S. Suzuki, J. Appl. Phys. **91**, 1314 (2002).
[7]C. Virojanadara and L. I. Johansson, Surf. Sci. Lett. **472**, L145 (2001).
[8]K. Y. Cheong, S. Dimitrijev, J. Han, and B. Harrison, J. Appl. Phys. **93**, 5682 (2003).
[9]P. Jamet and S. Dimitrijev, Appl. Phys. Lett. **79**, 323 (2001).
[10]K. McDonald, M. B. Huang, R. A. Weller, L. C. Feldman, J. R. Williams, F. C. Stedile, I. J. R. Baumvol, and C. Radtke, Appl. Phys. Lett. **76**, 568 (2000).
[11]C.-E. Morosanu, Thin Sold Films **65**, 171 (1980).
[12]K. McDonald, R. A. Weller, S. T. Pantelides, L. C. Feldman, G. Y. Chung, C. C. Tin, and J. R. Williams, J. Appl. Phys. **93**, 2719 (2003).
[13]S. Dhar, O. Seitz, M. D. Halls, S. Choi. Y. J. Chabal, and L. C. Feldman, J. Am. Chem. Soc. **131**, 16808 (2009).
[14]T. Shirasawa, K. Hayashi, S. Mizuno, S. Tanaka, K. Nakatsuji, F. Komori, and H. Tochihara1, Phys. Rev. Lett. **98**, 136105 (2007).
[15]T. Umeda, K. Esaki, R. Kosugi, K. Fukuda, T. Ohshima, N. Morishita, and J. Isoya, Appl. Phys. Lett. **99**, 142105 (2011).